NUMERICAL MODELING OF NO REDUCTION USING BIOMASS-BASED MATERIALS AS REBURN FUELS

Sumeet Bhalla and Sarma V. Pisupati
Department of Energy and Geo-Environmental Engineering
The Pennsylvania State University
110 Hosler Building
University Park, PA 16802

INTRODUCTION

The role of both homogenous and heterogeneous reactions in use of solid fuels such as coal for NO_x reduction has been discussed in some previous studies [1,2,3,4]. However Wendt [5], and Mereb and Wendt [6] have discounted heterogeneous reactions showing that they have minor contribution towards reburning. The reduction potential of a fuel depends on its ability to produce CH_i radicals to react with NO. Assuming only homogeneous gas phase reactions to participate in reduction, a higher volatile matter content of the fuel will enhance the NO_x reduction. In the recent past, the reburning process is reasonably well understood for use of coal and natural gas as reburn fuels [2, 3, 7, 8, 9, 10,11]. However pyrolysis products of biomass and biomass pyrolysis oils (bio-oils) have also been shown to cause NO_x reduction by mechanisms similar to reburning[12, 13]. Biomass and biomass based products offer the advantage of not only reduced SO_2, NO_x emissions because of low nitrogen and sulfur content but also reduced green house gases (N_2O and CO_2). However some fundamental questions such as the relative importance of homogeneous gas phase reactions in the process still need to be addressed.
In the present study, gas composition from flash pyrolysis of BioLime™ from an earlier study[14] was used to model NO reduction through homogeneous gas phase reactions when BioLime™ is used as a reburn fuel. The numerical predictions were then compared with the NO_x emissions from a down-fired combustor (DFC) to validate the model. A difference in NO_x reduction was observed by using two different BioLime™ samples as reburn fuel under similar operating conditions. This was believed to be due to difference in yield of flash pyrolysis products of the different BioLime™. With this in mind the model was further used to study the relative contribution of each of the pyrolysis gas species in NO reduction through homogeneous reactions. The predictions were then verified by experimental results from the flow reactor.

EXPERIMENTAL

Raw Materials
Two biomass based materials called BioLime™ I and III were obtained from DynaMotive Technologies Corporation. BioLime™ was produced by reacting pyrolysis oils from biomass with air, and lime/water slurry in a stirred. BioLime™ I and III had approximately 7 and 14 wt. % calcium, respectively. Compositional analysis of the samples is shown in Table 1.

	BioLime™ I (As Determined)	BioLime™ III (As Determined)
Carbon (wt. % daf)	48.5	38.7
Hydrogen (wt. % daf)	7.7	8.4
Nitrogen (wt. % daf)	0.23	0.21
Sulfur (wt. % daf)	0.01	0.02
Oxygen (wt. % daf by diff)	43.5	52.6
Ash (wt. % db)	20.9	48.5
Moisture (wt. %)	7.97	4.11

Table 1 Compositional analysis on as determined and dry basis for two BioLime™ samples

Down Fired Combustor
The DFC is 10 ft high with a 20-inch internal diameter rated at a nominal firing rate of 0.5 million Btu/h.. Several 4-inch sampling ports are located along the combustor. Sample ports are numbered 1 through 10 starting at the top. BioLime™ is introduced through port 5 into the reburn zone. The reburn zone parameters are shown in Table 2 . The flue gases from the heat exchanger pass through a pulse jet baghouse for particulate matter collection. The BioLime™ is prepared, stored in a day tank and pumped to the burner by a Moyno™ progressive cavity pump. The gaseous emissions data during the steady state was averaged.

DFC Reburn zone parameters	Values with the units
Diameter	50.8 cm
Total length	96.52 cm
Volume	195600 cm^3
Pressure	1 atm
Residence time	1.127 seconds
Inlet temperature at the center	1415 K
Inlet temperature at the wall	1426 K

Table 2 Down fired combustor reburn zone parameters

Modeling NO_x Reductions

All numerical calculations were done using a PSR computer code[15], which runs in conjunction with the Chemkin library[16]. The reverse rate constants were obtained from the forward rate constants and the thermodynamic data, mainly taken from the Sandia Thermodynamic Database[17]. The code computes species concentrations from the balance between the net rate of production of each species by chemical reaction and the difference between the input and output flow rates of species. The model used to predict NO emissions was taken from the studies of Kilpinen *et al.*[18], Glarborg *et al.*[19], and Prada and Miller[20]. In general the mechanism includes generation of hydrocarbon radicals from C_1 and C_2 parent hydrocarbons, oxidation mechanisms for HCN, and NH_3, together with a subset of the interactions between the hydrocarbon radicals and the nitrogenous species. The nitrogen-hydrocarbon chemistry is essentially an extension of the Miller and Bowman mechanism[21].

The procedure and assumptions in the above study are:

(1) Only homogeneous gas phase reactions are responsible for NO reduction. The effect of heterogeneous reactions is neglected. Gases from pyrolysis of BioLime™ react with NO_x in the reburn zone to form N_2 and nitrogenous intermediate species such as HCN and NH_3.
(2) Gas concentrations are calculated from the yields reported in an earlier study[14].
(3) Reburn fuel is mixed rapidly and perfectly with the products of combustion from the primary zone. This is achieved by use of high-pressure injection nozzle for feeding the reburn fuel.
(4) Reburn fuel is pyrolyzed instantly on entering the combustor and therefore pyrolysis kinetics does not control the NO_x reduction kinetics.
(5) The kinetics of reburning is controlled by the rate constants for the hydrocarbon-NO reaction system. The effect of mass transfer is neglected. This follows from the previous two assumptions.
(6) An average of the wall and bulk temperature at the point of reburn fuel injection is used as the inlet temperature for the calculations.
(7) Gas densities are calculated at the reburn zone inlet temperatures.
(8) The flue gas in reburn zone consists of 14% CO_2, 2.0% O_2, and 497 ppm of CO in nitrogen base. These concentrations of CO_2, O_2, and CO are chosen to be consistent with those of a coal primary flame operated at stoichiometric ratio of 1.0-1.1.
(9) A residence time of 1.127 seconds is used for the calculations, which is consistent with the residence time in reburn zone of the down-fired combustor.

RESULTS AND DISCUSSION

Predictions of NO_x emissions from the model along with the down-fired combustor data are shown in Table 3. The reburn zone stoichiometry was based on the total amount of fuel and oxidizer that entered the down fired combustor in the first two zones of the combustor divided by the stoichiometric requirement for the primary and reburn fuel[9]. The predictions from model match closely with the DFC data. The results showed a higher NO_x reduction for BioLime™ I than III. However, stoichiometry was different for different runs when BioLime™ I and III are used as reburn fuel. Therefore, to further compare the performance of BioLime™ I and III, NO_x reduction was estimated for both BioLime™ for each run. The results are shown in Figure 1. It can be seen that BioLime™ I produced a higher NO_x reduction than BioLime™ III, and is attributed to the higher yield of total pyrolysis gases for BioLime™ I. These results are in agreement with the studies of Kicherer *et. al.* [22], who have shown that the main reduction effect is due to the volatiles of the reburning fuel. Therefore, a higher yield of pyrolysis gases will result in a higher NO_x reduction. Different pyrolysis gases can have different NO_x reduction potential. However as seen from Table 3, the relative percentage of pyrolysis gases added was different for different runs. Knowledge of relative contribution of pyrolysis gases in NO_x reduction would help to choose a biomass feedstock that increases the yield of desired species. With this in mind a parametric analysis is done using the model to study the effect of varying concentration of hydrocarbons, CO_2, CO, H_2.

Run (BioLime™)	Stoichiometry	% of Hydro carbon added	% CO_2 added	% CO added	% H_2 added	% NO_x Reduction (DFC)	% NO_x Reduction (Model)
Run 1(I)	0.501	0.13	14.88	0.25	0.23	17.0	16.0
Run 2(I)	0.517	0.14	14.92	0.26	0.24	16.2	16.8
Run 3(III)	0.549	0.09	14.50	0.18	0.20	13.6	11.2
Run 4(III)	0.652	0.04	14.20	0.10	0.08	11.6	4.4
Run 5(III)	0.656	0.05	14.27	0.12	0.11	12.5	7.2
Run 6(III)	0.717	0.05	14.27	0.12	0.11	12.6	6.3

Table 3. Model predictions for percentage NO_x reduction with NO_x reduction from DFC.

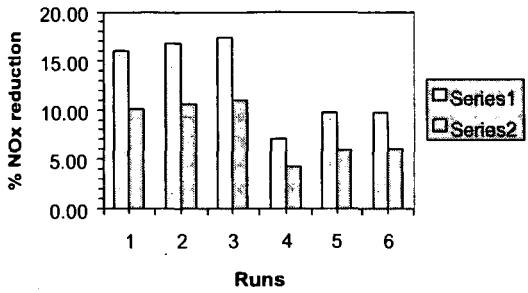

Figure 1. Influence of BioLime™ used on NO_x reduction. The % NO_x reduction is predicted from model for both BioLime™ for each run condition.(Series 1 – BioLime™ I, Series 2 - BioLime™ III)

The results were then verified using the flow reactor. The setup of the flow reactor is discussed in an earlier study[14]. CO_2, CO, and H_2 had very little effect on NO_x reduction. Hydrocarbons were seen to be mainly responsible for causing reduction in emissions of NO_x. Kilpinen *et. al.* [23], Chen *et. al.* [24] , Mereb and Wendt [25] have also shown that for natural gas reburning CO, and H_2 are useable as reburn fuels, even though the rates of reaction for NO reduction by CO and H_2 are significantly slower compared to NO-hydrocarbon reactions. Two main stages are considered to be mainly responsible for nitric oxide reduction. First is the conversion of NO to HCN, through reaction with CH_i and HCCO.

$$NO + HCCO \quad HCNO + H \quad HCN$$
$$NO + CH_2 \quad HCN + OH$$
$$NO + CH_3 \quad H_2CN + M \quad HCN$$
$$NO + CH_3 \quad HCN + H_2O$$

The second stage is the reaction of HCN with the oxidizing species (O, OH) to form NH_i, N_2, and NO. HCN is first converted to isocyanic acid and HNCO primarily by

$$HCN + OH \quad HOCN + H \quad HNCO$$

and to a lesser extent also through the direct reaction

$$HCN + OH \quad HNCO + H$$

The HNCO reacts further to NH_2. This occurs primarily by the reaction with H radical

$$HNCO + H \quad NH_2 + CO$$

The NH_2 radical depending on the conditions can be converted to N_2, NH_3, or NO.

Burch *et. al.* [26] in their study of different fuels (methane, hexane, benzene, and coal) have also shown that NO_x reduction efficiency can also be related to C/H ratio for the fuel. Carbon rich fuels produce more CH_i fragments, leading to a lower NO_x concentration. BioLime™ I had a C/H ratio of 6.3 whereas BioLime™ III had a C/H ratio of 4.6. Therefore, a BioLime™ with a higher C/H ratio will help to increase the NO_x reduction.

CONCLUSIONS

1) Percentage of NO_x reduction using BioLime™ as a reburn fuel was accurately predicted using the homogeneous gas phase reaction model. For most of the conditions, the percentage NO_x reduction predicted from model was well within the allowable variation from the experimental results from down fired combustor and flow reactor. However in some studies like those of Smart and Morgan [27], Chen and Ma [28] have also shown the role of char reactions in NO_x reduction.
2) The higher NO_x reduction potential of BioLime™ I over BioLime™ III was attributed to the higher yield of total pyrolysis gases.
3) The parametric study from flow reactor showed that the CO, CO_2, and H_2 have very little effect and hydrocarbon reactions are mainly responsible for NO_x reduction. Hence a fuel with higher C/H ratio will produce more CH_i fragments, and therefore, result in a better NO_x reduction.

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